Quantum Zeno Effect in Radical-Ion-Pair Recombination Reactions

I. K. Kominis

Department of Physics, University of Crete, Heraklion 71103, Greece and
Institute of Electronic Structure and Laser, Foundation for Research and Technology, Heraklion 71110, Greece
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Radical-ion pairs are ubiquitous in a wide range of biochemical reactions, ranging from photosynthesis to magnetic sensitive chemical reactions underlying avian magnetic navigation. We here show that the charge recombination of a radical-ion-pair is a continuous quantum measurement process that interrogates the spin state of the pair. This naturally leads to the appearance of the quantum Zeno effect, explaining a large amount of data on unusually long-lived radical-ion-pairs.

Radical-ion pairs are playing a fundamental role in a series of biologically relevant chemical reactions, ranging from charge transfer initiated reactions in photosynthetic reaction centers [1] to magnetic sensitive reactions abounding in the field of spin-chemistry [2], and in particular in the biochemical processes understood to underlie the biological magnetic compass of several species having the ability to navigate in earth's magnetic field [3, 4].

In Fig. 1 we depict a generic model for the radical-ion-pair (RIP) creation and recombination dynamics. A donor-acceptor molecule DA is photo-excited (D*A) and a subsequent charge-transfer creates the RIP (D$^+$A$^-$). The singlet and triplet states of the RIP (^{1}D$^+$A$^-$, ^{3}D$^+$A$^-$) are split by internal magnetic interactions of the RIP's two unpaired electrons with external magnetic fields and internal hyperfine couplings. The RIP is initially created in the singlet state, which is not an eigenstate of the magnetic Hamiltonian, and therefore a singlet-triplet (S-T) coherent mixing commences. The RIP eventually tunnels into an excited state of the neutral recombined molecule DA, which quickly decays into the ground state. As is well known [5, 6], electron transfer in RIP recombination reactions is fundamentally a quantum-mechanical tunneling process. In this Letter we will show that this process constitutes a continuous quantum measurement of the RIP's spin state. Like every quantum measurement, this one is no exception to the rule that measurements performed on a quantum system lead to decoherence [7]. However, under appropriate conditions involving the measurement rate and the intrinsic frequency scale of the RIP, the quantum Zeno effect [8] appears and leads to two physically significant consequences: (i) dephasing rates of the RIP S-T coherent mixing are suppressed, and (ii) the RIP's spin state is delocalized, i.e. there is a high probability of triplet state occupation even if the singlet and triplet states are non-degenerate.

Quantum Zeno effects appear in several physical systems, some of which are very similar to radical-ion-pairs, like the ortho-para conversion in molecular spin isomers [10], ultra-cold atom tunneling through optical potentials [11], or the suppression of transverse spin-relaxation due
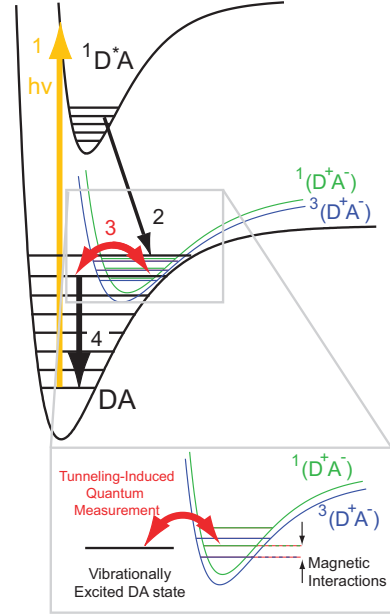

FIG. 1: Generic level structure and recombination dynamics in a radical-ion-pair, taking place in four steps: 1, photoexcitation, 2, RIP creation, 3, tunneling-induced quantum measurement of RIP's spin state and 4, final decay to the ground state.

to spin-exchange collisions in dense alkali-metal vapors [12, 13]. In the latter case, atomic spin-exchange collisions, of the form $\mathbf{s}_1 \cdot \mathbf{s}_2$, where $\mathbf{s}_1$ and $\mathbf{s}_2$ are the electron spins of the two colliding atoms, probe the atomic spin state. When the collision rate (measurement rate) exceeds the intrinsic frequency scale of the system, which is the Larmor frequency of spin precession in the applied magnetic field, the effective decay rate of the spin coherence is suppressed, a phenomenon that has led to the development of new ultra-sensitive atomic magnetometers [14]. The RIP tunneling into the neutral state is essentially a scattering process [15], not unlike atomic collisions, that performs a measurement of the RIP's spin state, since tunneling can only proceed if the RIP is in the singlet spin state. Quantum Zeno effects have been extensively analyzed in the literature [16, 17, 18, 19], both

with respect to pertaining physical systems, as well the general conditions leading to the quantum Zeno effect or its inverse, the anti-Zeno effect [20, 21, 22].

In the following, we are going to capitalize on the remarkably strong analogy between radical-ion-pairs and yet another physical system, namely two coupled quantum dots [23, 24, 25, 26, 27] being continuously interrogated by a point contact. We are going to identify the analogous physical observables of the two systems and then setup the corresponding evolution equation describing the RIP state, in order to directly arrive at the basic physical results. The electron hopping between the two dots is the analog of the S-T coherent mixing taking place in the RIP, whereas the measurement performed by the point contact corresponds to the spin-state-dependent RIP tunneling into an adjacent excited state of the recombined DA molecule.

We will consider the simplest possible RIP model, in which the triplet-state manifold is degenerate (and defines the zero energy), and the singlet state has energy ω:

$$\mathcal{H}_{\mathrm{RIP}} = \omega c_S^\dagger c_S + \Omega(c_S^\dagger c_T + c_T^\dagger c_S) \qquad (1)$$

where Ω is the S-T mixing frequency. The tunneling to a nearby excited DA state $|a\rangle$ with energy ω_a can only occur if the RIP is in the singlet state, hence the tunneling Hamiltonian is

$$\mathcal{H}_{\mathrm{T}} = T_{\mathrm{Sa}} c_S^\dagger a + T_{\mathrm{Sa}}^* c_S a^\dagger, \qquad (2)$$

where T_{Sa} is the tunneling amplitude. This Hamiltonian embodies angular momentum conservation in the tunneling process, i.e. the tunneling amplitude for the triplet state is zero. In reality, the tunneling Hamiltonian is more complicated, since there are several resonant vibrational states $|a\rangle$, and the recombination rate is given by [5]

$$k = (2\pi/\hbar)|V|^2 \sum_a |f_{S,a}|^2 \delta(\omega - \omega_a) \qquad (3)$$

where V is the electronic matrix element and $f_{S,a}$ the vibrational overlap between the nuclear wavefunctions of $|a\rangle$ and the singlet state of the RIP. In this realistic case, the tunneling Hamiltonian becomes

$$\mathcal{H}_{\mathrm{T}} = \sum_a T_{\mathrm{Sa}} c_S^\dagger a + T_{\mathrm{Sa}}^* c_S a^\dagger, \qquad (4)$$

where now $T_{\mathrm{Sa}} = V f_{S,a}$.

Finally, the Hamiltonian of the DA excited state will be $\mathcal{H}_a = \omega_a a^\dagger a$. The operators c_S $(c_S^\dagger)$, c_T $(c_T^\dagger)$ and a $(a^\dagger)$ are electron annihilation (creation) operators for the single-electron states $|S\rangle$, $|T\rangle$ and $|a\rangle$, respectively. The rate constant k is termed the recombination rate, and will be later identified with observable rate constants. The complete interaction Hamiltonian governing the time evolution of the combined system is then

$\mathcal{H} = \mathcal{H}_a + \mathcal{H}_{\mathrm{RIP}} + \mathcal{H}_{\mathrm{T}}$. The same set of Hamiltonians has already been treated at [24]. In similar fashion, it is readily shown that by tracing out the $|a\rangle$ degrees of freedom, we arrive at the dissipative evolution of the RIP density matrix ρ:

$$\frac{d\rho}{dt} = -i[\mathcal{H}_{\mathrm{RIP}}, \rho] - k\mathcal{D}[c_S^\dagger c_S]\rho \qquad (5)$$

where the super-operator $\mathcal{D}[B]$ acts on the density matrix ρ according to

$$\mathcal{D}[B]\rho = B^\dagger B\rho + \rho B^\dagger B - 2B\rho B^\dagger \qquad (6)$$

The occupation number $c_S^\dagger c_S$ can also be written as $Q_S = 1/4 - \mathbf{s}_1 \cdot \mathbf{s}_2$, which is the singlet-state projection operator in a RIP with the unpaired electron spins being $\mathbf{s}_{1,2}$. In other words, the eigenvalues of Q_S are 1 (RIP in the singlet state) and 0 (RIP in the triplet state). Since $Q_S^\dagger = Q_S$ and $Q_S^2 = Q_S$, we arrive at the evolution equation

$$\frac{d\rho}{dt} = -i[\mathcal{H}_{\mathrm{RIP}}, \rho] - k[Q_S, [Q_S, \rho]] \qquad (7)$$

This is exactly the evolution equation that follows from standard quantum measurement theory [7, 28], when the measured observable is Q_S and the measurement rate is k. We can generalize this by opening a triplet recombination channel, with a recombination rate k_T (the singlet recombination rate, so far denoted by k is renamed k_S). It is readily shown (since $Q_S + Q_T = 1$) that the evolution equation is again given by (7), with $k = k_S + k_T$.

In the simple two-dimensional RIP model we are considering, the density matrix, the Hamiltonian and the singlet-state projection operator are 2×2 matrices:

$$\rho = \begin{pmatrix} \rho_{SS} & \rho_{ST} \\ \rho_{TS} & \rho_{TT} \end{pmatrix}, \ \mathcal{H}_{\mathrm{RIP}} = \begin{pmatrix} \omega & \Omega \\ \Omega & 0 \end{pmatrix}, \ Q_S = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \ (8)$$

The evolution equation (7) can compactly be written as $d\rho/dt = \mathcal{L}(\rho)$, where $\mathcal{L}$ is a super-operator. The complex eigenvalues of the matrix A resulting from the requirement $\mathcal{L}(\rho) = A\rho$ (where ρ is now a column vector $(\rho_{SS} \ \rho_{ST} \ \rho_{TS} \ \rho_{TT})^T$) are of the form $-\lambda + i\omega_e$, where $\lambda \geq 0$ is the decay rate and ω_e is the effective mixing frequency. In the simple system we are considering, there are three independent density matrix elements, and hence three eigenvalues. These are shown in Fig.2 as a function of the recombination rate k (normalized to the unperturbed mixing frequency Ω). Out of the three decay rates, two (degenerate ones) increase with k and are termed "normal"; the quantum Zeno effect is manifested in two ways: (i) the third decay rate, λ_{qZ}, is suppressed with increasing measurement rate k, and (ii) the effective mixing frequency drops in the limit of strong measurement (large k). The scaling of λ_{qZ} with the measurement rate k is $\lambda_{\mathrm{qZ}} \sim \Omega^2/k$. This scaling is typical of quantum Zeno effects [16, 20, 29], since the Zeno time τ_Z is in this
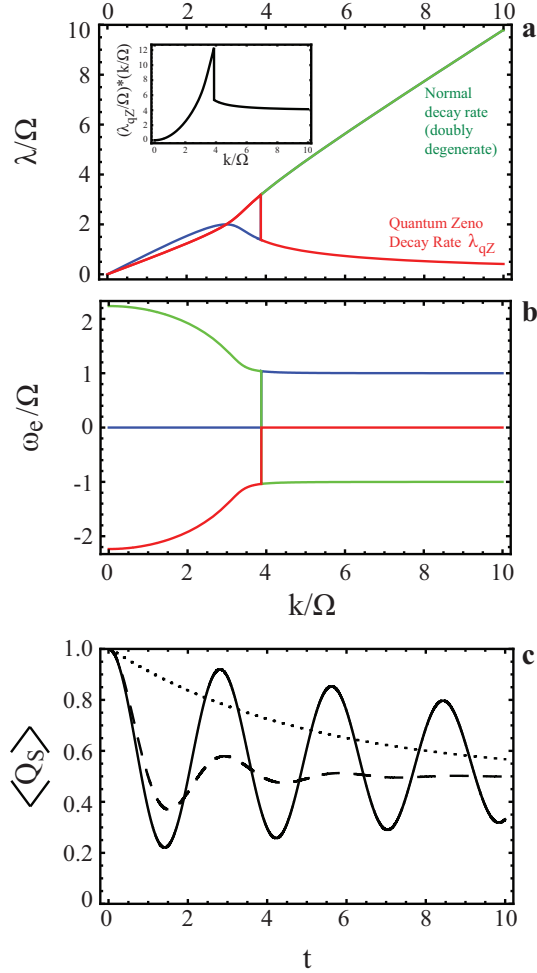
FIG. 2: Decay rates and eigenfrequencies of the evolution equation. (a) The "normal" decay rates are the ones that increase with the measurement rate k. Quantum Zeno effect appears in the decay rate that is suppressed with k, denoted by λ_{qZ}, which is shown in the inset to be $\lambda_{qZ} \approx 4\Omega^2/k$ at high k.(b) Corresponding eigenfrequencies.The eigenfrequencies at high measurement rates are smaller than at low rates, an effect well-known from spin-exchange relaxation collisions in dense alkali-metal vapors [12]. In both (a) and (b) $\omega/\Omega = 1$. (c) The expectation value $\langle Q_S \rangle$ for $\rho(t=0) = Q_S$, $\omega = \Omega = 1$ and $k = 0.1$ (solid line), $k = 1$ (dashed line) and $k = 20$ (dotted line).

case given by $\tau_Z^{-1} = \sqrt{\langle S|\mathcal{H}_{\mathrm{RIP}}^2|S\rangle - \langle S|\mathcal{H}_{\mathrm{RIP}}|S\rangle^2} = \Omega$, i.e. $\lambda_{qZ} = \tau/\tau_Z^2$, where $\tau = 1/k$. The long-lived eigenvalue λ_{qZ} will determine the long-time behavior of the density matrix elements. A typical value of the recombination rate is $k \approx 1$ ns^{-1}. For an unperturbed mixing frequency $\Omega \approx 30$ ns^{-1} (this corresponds to a hyperfine coupling of 10 G), we find that $\lambda_{\mathrm{qZ}} \approx 1$ μs^{-1}. The lifetime of the S-T mixing process can thus be prolonged by several orders of magnitude.

This naturally explains several experimental observations regarding long-lived radical-ion pairs [30, 31, 32]. It should be noted that by "recombination" rate we re-

fer to the fast-decaying eigenmodes of the density matrix, i.e. those for which the decay rate scales proportionally with k. Time scales on the order of 10 ps-1 ns, which govern the creation of the RIP through photoexcitation and decay of the excited DA-state could so far not be fathomed with long-lived radical-ion-pairs, i.e. since the D*A-RIP and RIP-DA energy differences are comparable, why doesn't the RIP disappear at sub-ns time scales? This cannot be explained by the presence of the "metastable" triplet state, since the mixing rates with the singlet state are typically in the 10 ns timescale. Therefore, even if the RIP is created in the triplet state, it should disappear fast through T-S mixing and singlet-channel charge recombination. The quantum Zeno effect naturally leads to RIP lifetimes that extend even to the μs timescale. The theoretical models that were used until now [33, 34, 35, 36] to describe RIP recombination dynamics masked the presence of the quantum Zeno effect, since they treated the tunneling process of the RIP and the subsequent decay to the DA ground state (steps 3 and 4 in Fig. 1) with a single, phenomenological density matrix equation $d\rho/dt = -i[\mathcal{H}_{\mathrm{RIP}}, \rho] - k(\rho Q_S + Q_S \rho)$. This equation accounts for the depopulation of the singlet RIP state at a rate $2k$, i.e. the probability $S = \mathrm{Tr}\{\rho Q_S\}$ to find the RIP in the singlet state decays exponentially at a rate $2k$, unavoidably inducing a simultaneous dephasing of the S-T coherent mixing at the the high rate k. It is noted for completeness that the aforementioned semiclassical density matrix equation leads to similar results just in this particular two-dimensional toy-model of the RIP. As soon as we move to a realistic description of the RIP, which involves at least an 8-dimensional density matrix (4 is the two-electron spin multiplicity and 2 the spin multiplicity of one nucleus with spin-1/2, which is the bare minimum needed to form a RIP supporting singlet-triplet mixing), all decay rates scale proportionally to k and there is no manifestation of the Zeno effect. This is not the case with the density matrix equation (7).

The second physical consequence of the quantum Zeno effect in the RIP recombination merits some discussion. The probability for significant triplet state population is high, on the order of unity, even for S-T energy differences $\omega > \Omega$. This effect has been discussed in [23], and in the simple RIP model we are considering, it is seen in the fact that ρ_{SS} tends to 1/2 in the long-time limit, irrespective of the problem's frequencies. This has tangible consequences, since in realistic systems, the triplet state RIP can recombine to other chemical products, or in cases of RIPs in solution, the D and A molecules will eventually diffuse away. In both cases, a large probability of populating the RIP triplet state will be evident in the reduced yield of recombined DA molecules.

We will finally elaborate on step 4 of Fig.1, namely the decay to the ground state of the neutral DA molecule. The continuous quantum measurement performed by the tunneling process into the excited DA state will at times

be interrupted when there is a definite measurement outcome. This is described by the quantum-jump approach [24, 37] of the quantum-trajectories description of dissipative quantum systems. When the outcome of measuring Q_S is 1, that is, the RIP is in the singlet state for sure, tunneling and decay to the DA ground state can proceed. This is formally described by the conditional evolution of the RIP's quantum state $|\Psi\rangle$,

$$
\begin{aligned}
|\Psi(t+dt)\rangle = |\Psi(t)\rangle &- idt\mathcal{H}_{RIP}|\Psi(t)\rangle \\
&- kdt(Q_S - \langle Q_S\rangle)|\Psi(t)\rangle \\
&+ dN\left(Q_S/\sqrt{\langle Q_S\rangle} - 1\right)|\Psi(t)\rangle \quad (9)
\end{aligned}
$$

The stochastic point process that takes the values 0 and 1, i.e. $(dN)^2 = dN$, and $M[dN] = 2k\langle Q_S\rangle dt$, where $M[.]$ represents the mean over all possible realizations of the process. The first three term in (9) represent the no-jump deterministic evolution of the RIP state, while the last term describes the quantum jump that eventually occurs opening the possibility for charge recombination, after which the DA molecule can relax to its ground state. This way we have closed the excitation-recombination cycle pictured in Fig. 1. Analogously to the tunneling current [24, 26] we can define a "charge-recombination current" $R_c = dN/dt = k\langle Q_S\rangle$. The recombination reaction rates can then be defined as the characteristic rates appearing in the two-time correlation function $G(\tau) = E[R_c(t)R_c(t+\tau)]$, which is similarly to [24, 26] shown to be given by $G(\tau) = k^2(\text{Tr}\{e^{\mathcal{L}\tau}\rho_{s,\infty}\} - 1/4)$, where $\rho_{s,\infty} = Q_S\rho_\infty Q_S$ is the singlet projection of the steady state density matrix (which in this case is $\rho_\infty = 1/2$). Thus the reaction rates are the eigenvalues of $\mathcal{L}$ that we have calculated and plotted in Fig. 1.

In summary, starting from first principles, we have here demonstrated the fundamentally quantum-mechanical nature of the radical-ion-pair recombination process. This provides a natural explanation of several unusual experimental findings in RIP chemical reactions. More important, it is not inconceivable that quantum Zeno effects in radical-ion-pairs could be found to be intimately involved with the quantum-mechanical foundations of photosynthetic reactions.

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